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Cosmetic.

A cosmetic composition acts as a film former resistant to various effects and comprises a copolymer of a fluoroalkyl (meth)acrylate and a long chain, linear alkyl (meth)acrylate. It may further comprise a volatile oil one or more solid fats.

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COSMETIC

This invention relates to a cosmetic. More particularly, it relates to a cosmetic causing no irritation on the skin which contains copolymer(s) of long-chain alkyl (meth)acrylate(s) with
5 (meth)acrylate(s) having a bonded fluoroalkyl group readily soluble in volatile oil for cosmetics as a film-forming component which makes said cosmetic resistant against water, oil and physical friction.

Statement of Prior Arts

Conventional cosmetics may be classified into those of aqueous, nonaqueous, emulsion and powder types. Among them, aqueous, emulsion and powder
5 cosmetics are deteriorated by moisture such as sweat, tear, rain or snow, while emulsion, powder and nonaqueous ones are deteriorated by oil such as sebum and oily components of foods and drinks. Further each of them is deteriorated by physical
10 friction with, for example, clothes or cups, which makes it impossible to maintain its makeup effect.

Thus it has been attempted to add polymer(s) to a cosmetic to thereby form a film on the skin after applying the cosmetic thereon, thus improving
15 the adhesion between pigment and solid fat contained in the cosmetic and the skin and prolonging the duration of the makeup effect.

In order to achieve this object, it has been mainly attempted to develop aqueous or emulsion
20 type of cosmetics containing water-soluble polymers

such as vinyl acetate or acrylic polymers as a film-forming component or nonaqueous type of cosmetics wherein oil-soluble polymers such as rosin, shellac or alkylcellulose are added as a film-
5 forming component with a solvent.

However the film of a cosmetic containing water-soluble polymer(s) exhibits an unsatisfactory water resistance although it is highly resistant against oil and physical friction. Further it is
10 difficult to prepare rigid solid products such as sticks or pencils from aqueous or emulsion type of cosmetics. On the other hand, a cosmetic containing oil-soluble polymer(s) may be blended with solid fat to thereby form a solid product such as a stick or
15 a pencil. The solid product thus produced forms a film which exhibits an excellent water resistance and a poor oil resistance. Conventional oil-soluble polymers such as rosin, shellac or alkylcellulose can not be dissolved in volatile oil for
20 cosmetics such as low-boiling point hydrocarbons or dimethylpolysiloxane at room temperature so that cosmetics containing the same can not be homogeneously spread on the skin or mucosa. Thus these cosmetics give an unsatisfactory touch in application

and poor adhesion to the skin or mucosa and exhibit a poor frictional resistance. In addition, many natural resins including rosin and shellac would show a sensitizing activity, which brings about a
5 problem from the viewpoint of safety. Thus conventional cosmetics containing polymer(s) are far from satisfactory from various viewpoints including the duration of the makeup effect, touch, and obtained makeup condition.

10 Therefore it has been required to develop a cosmetic containing highly safe polymer(s) which forms a film resistant against physical friction as well as water and oil and can be homogeneously dissolved in a solvent used for cosmetics while
15 undergoing no decrease in the touch. It is also expected that such an cosmetic can be formulated into a solid product such as a stick or a pencil.

Summary of the Invention

The invention provides a cosmetic containing as
20 a film-forming agent a copolymer(s) of a long chain alkyl (meth)acrylate(s) and a fluoroalkyl (meth)acrylate(s). It may further comprises a volatile oil.

The invention moreover provides a cosmetic composition comprising an oil-soluble polymer, a volatile oil having a boiling point of not higher than 280°C and solid fat(s) having a penetration of
5 not higher than 40.

The copolymer to use in the invention is highly safe and readily soluble in a solvent mixture of low-boiling point hydrocarbons containing a large amount of highly safe volatile oil for cosmetics,
10 such as a cyclic dimethylpolysiloxane, exhibits an excellent water resistance as well as an excellent oil resistance because of the presence of fluorine moiety in the copolymer(s) when applied to the skin, can be homogeneously spread on the skin
15 because of its high solubility in solvents and forms a film showing satisfactory adhesion and a high frictional resistance.

We have further found that the abovementioned polymer(s) is oil-soluble and readily soluble in a
20 solvent so that it may be formulated into solid products such as oily sticks or pencils having an

extremely preferable touch and that the film-forming property of the polymer(s) and the effect of maintaining the makeup condition of the obtained film are both satisfactory, thus completing the present invention.

Accordingly, the present invention provides a cosmetic characterized by containing one or more copolymers of long-chain alkyl (meth)acrylate(s) with (meth)acrylate(s) having a bonded fluoroalkyl group as a film-forming component.

Preferable examples of the long-chain alkyl (meth)acrylate used in the present invention are esters of straight-chain or branched alkyl alcohols having eight or more carbon atoms, e.g. long-chain alcohols such as octyl, decyl, lauryl, cetyl, stearyl or behenyl alcohol with (meth)acrylic acid. Esters of long-chain alcohols having 18 or more carbon atoms are particularly preferable.

Examples of the (meth)acrylate having a bonded fluoroalkyl group are known compounds having a bonded polyfluoroalkyl or perfluoroalkyl group, such as $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_6\text{F}_{13}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_8\text{F}_{17}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_{10}\text{F}_{21}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_{12}\text{F}_{25}$,

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_6\text{F}_{13}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_8\text{F}_{17}$,
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_{10}\text{F}_{21}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_{12}\text{F}_{25}$,
 $\text{CH}_2=\text{CHCOOC}_2\text{H}_4-(\text{CF}_2)_6-\text{H}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4-(\text{CF}_2)_8-\text{H}$,
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4-(\text{CF}_2)_6-\text{H}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4-$
 5 $(\text{CF}_2)_8-\text{H}$.

In the present invention, one or more compounds obtained by copolymerizing these long-chain alkyl (meth)acrylate(s) with (meth)acrylate(s) having a bonded fluoroalkyl group may be employed.

10 The long-chain alkyl (meth)acrylate and (meth)acrylate having a bonded fluoroalkyl group may be copolymerized preferably in a ratio by weight of 10 : 1 to 1 : 5, still preferably 7 : 1 to 1 : 1, considering the relationship between the
 15 solubility and stickness.

The copolymer may contain a third monomer unit.

The molecular weight of the copolymer may be preferably 1000 to 2,000,000, still preferably 10,000 to 500,000, considering the relationship
 20 between the frictional resistance and stickness of the same.

In addition to the copolymer(s) of long-chain alkyl (meth)acrylate(s) and (meth)acrylate(s)

having a bonded fluoroalkyl group, which are the essential components, the cosmetic of the present invention may further contain conventional components such as various volatile and nonvolatile
5 oils, surfactants, wetting agents, preservatives, antioxidants, perfumes and powder constituents if required.

The volatile oil preferably includes straight or branched hydrocarbons and cyclic dimethylpolysiloxanes,
10 each having a boiling point of not higher than 260°C. Examples of the nonvolatile oils are straight-chain or branched hydrocarbons optionally unsaturated, synthetic ester oils derived from higher alcohols and fatty acids, higher alcohols, higher fatty
15 acids and waxes. Examples of the surfactants are polyoxyethylene alkyl ethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, sorbitan fatty acid esters, glycerol fatty acid esters, polyoxyethylene hardened castor oil
20 and polyoxyethylene sorbitol fatty acid esters. Examples of the wetting agents are sorbitol, glycerol, propylene glycol, 1,3-buthylene glycol,

maltitol, lactic acid, sodium lactate and polyethylene glycol. Examples of the preservatives are alkyl p-hydroxybenzoates, sodium benzoates, potassium sorbate and phenoxyethanol. Examples of the
5 antioxidants are tocopherol, sesamol, sesamolin and lecithin. Examples of the powder constituents are titanium oxide, zinc oxide, ultramarine blue, chromium oxide, iron oxide, talc, sericite, mica, kaolin, micaceous titanium and organic pigments.

10 The cosmetic of the present invention may furthermore contain conventional film-forming component(s) such as various resins including acrylate and vinyl acetate resins in addition to the copolymer(s) of the invention depending on the
15 form of the products.

The copolymer(s) of long-chain alkyl (meth)acrylate(s) with (meth)acrylate(s) having a bonded fluoroalkyl group are contained in the cosmetic of the present invention preferably in
20 an amount of 0.1 to 70% by weight, more preferably 0.5 to 40% by weight, of the total cosmetic. A content of the same lower than 0.1% by weight might result in a poor film-forming effect, while a

content of the same exceeding 70% by weight might sometimes result in insufficient dispersion caused by an unbalanced composition.

When the composition contains a volatile oil, it
5 contains 0.1 to 50 wt.%, preferably 1 to 30 wt.%, based on the oil, of the copolymer.

The cosmetic of the present invention may be prepared by, for example, mixing the essential components, i.e. copolymer(s) of long-chain alkyl
10 (meth)acrylate(s) and (meth)acrylate(s) having a bonded fluoroalkyl group, and other components, if any, by heating with the use of, e.g., a homomixer, a homodisperser or a three-roll mixer and formulating the mixture into a desired form if required.

15 The cosmetic of the present invention may be appropriately used as a skin cosmetic and formulated into various makeup products such as foundation, lipstick, eyeliner, mascara, eyebrow or rouge.

These skin cosmetics may be prepared by mixing the
20 film-forming components comprising the above-mentioned copolymer(s) with volatile and nonvolatile oils including solid fats as well as other desired components by heating with the use of, for example, a homomixer, a homodisperser or a three-

roll mixer and formulating the mixture into desired forms. Thus oily solid cosmetics such as sticks or pencils having excellent proprieties can be obtained.

5 Then the invention will be explained in reference to the second embodiment thereof. It provides an oily solid cosmetic characterized by essentially containing oil-soluble polymer(s), volatile oil(s) having a boiling point of not higher than 280°C and solid having
10 a penetration. (JIS K-2530' 25°C, 100g, 5 sec) of not higher than 40.

 The relationship among the oil soluble polymer(s) the volatile oil(s) and the solid fat(s) each used in the present invention is as follows. That is,
15 the oil-soluble polymer(s) are soluble or dispersible

in the volatile oil(s) but incompatible with the solid fat(s) and the solid fat(s) is insoluble in the volatile oil(s) at a temperature not higher than 40°C.

Examples of the volatile oil(s) used in the present invention are those having a boiling point not higher than 280°C, such as straight-chain dimethylpolysiloxane of a viscosity of 0.5 to 10 cSt (25°C), cyclic dimethylpolysiloxane having a three- to six-membered ring and straight-chain or branched hydrocarbons having three to 16 carbon atoms and optionally unsaturated. One of these oils may be employed. Alternately a mixture thereof may be used.

Examples of the solid fat(s) having a penetration (JIS K-2530; 25°C, 100g, 5 sec) not higher than 40 used in the present invention are those conventionally used for cosmetics, such as hydrocarbons having a melting point not lower than 40°C, waxes including synthetic esters derived from alcohols and fatty acids, natural waxes, higher alcohols and higher fatty acids. One of these materials may be used. Alternately a mixture thereof may be employed. It is particularly preferable to use those having a penetration (JIS K-2530; 25°C, 100g, 5 sec) of 0.5 to 20.

The oil-soluble polymers used in the present invention are those soluble or dispersible in the

volatile oils and incompatible with the solid fats.

Preferable examples are as follows.

First, polymers or copolymers of vinyl monomers having a side chain comprising a long-chain alkyl group
5 having eight or more carbon atoms, such as (meth)-acrylates, maleates and fumarates of long-chain alkyl alcohols, vinyl ethers, vinyl esters of higher fatty acids or α -olefins may be preferably used. Long-chain alkyl groups having eight to 22 carbon atoms are
10 particularly preferable. More particularly, polystearyl acrylate, polybehenyl acrylate, polystearyl methacrylate, polybehenyl methacrylate, polystearyl vinyl ether, polyvinyl stearate, C_{12} - α -olefin/distearyl maleate copolymer and C_{12} - α -olefin/distearyl fumarate copolymer
15 may be cited. Those having a molecular weight of 5,000 to 2,000,000 are particularly preferable.

Secondly, rubber-like polymers such as polyisoprene, ethylene/propylene rubber, polybutadiene and ethylene/vinyl acetate copolymer may be cited.

20 In addition, copolymers of alkyl (meth)acrylates having an alkyl group having eight or more carbon atoms with (meth)acrylates having a bonded fluoroalkyl group may be employed. Examples of the alkyl (meth)-acrylates having an alkyl group having eight or more
25 carbon atoms include esters of octyl, decyl, lauryl,

cetyl, stearyl or behenyl alcohol with (meth)acrylic acid. Any copolymer may be employed so long as it can be copolymerized. It is particularly preferable to use (meth)acrylate comonomers having a bonded

- 5 fluoroalkyl group. Examples of the (meth)acrylates having a bonded fluoroalkyl group include well-known compounds having a polyfluoroalkyl or perfluoroalkyl group, such as $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_6\text{F}_{13}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_8\text{F}_{17}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_{10}\text{F}_{21}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_{12}\text{F}_{25}$,
 10 $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_6\text{F}_{13}$, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_8\text{F}_{17}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_{10}\text{F}_{21}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{C}_{12}\text{F}_{25}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4-(\text{CF}_2)_6\text{H}$, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4-(\text{CF}_2)_8\text{H}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4-(\text{CF}_2)_6\text{H}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4-(\text{CF}_2)_8\text{H}$.

These long-chain alkyl (meth)acrylates may be

- 15 copolymerized with the (meth)acrylates having a bonded fluoroalkyl group in a ratio by weight of 10 : 1 to 1 : 5 considering the solubility, dispersability and stickiness thereof.

- One or more oil-soluble polymers as mentioned
 20 above may be employed in the present invention.

- The oily solid cosmetic of the present invention may further contain various components conventionally used in the art, such as nonvolatile oils, surfactants, wetting agents, preservatives, antioxidants, perfumes
 25 or powder constituents, in addition to the essential

components as described above.

Examples of the nonvolatile oil are straight-chain or branched hydrocarbons optionally unsaturated, synthetic ester oils derived from higher alcohols and 5 fatty acids, and lecithin.

Examples of the surfactants are polyoxyethylene alkyl ethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, sorbitan fatty acid esters, glycerol fatty acids esters, 10 polyoxyethylene hardened castor oil and polyoxyethylene sorbitol fatty acid esters. Examples of the wetting agents are sorbitol, glycerol, propylene glycol, 1,3-butylene glycol, maltitol, lactic acid, sodium lactate and polyethylene glycol. Examples of the 15 preservatives are alkyl p-hydroxybenzoates, sodium benzoate, potassium sorbate and phenoxyethanol. Examples of the antioxidants are tocopherol, sesamol and sesamolin. Examples of the powder constituents are titanium oxide, zinc oxide, ultramarine blue, chromium 20 oxide, iron oxide, talc, sericite, mica, kaolin, micaceous titanium and organic pigments.

The volatile oil(s) may be contained in the oily solid cosmetic of the present invention preferably in an amount of 5 to 80% by weight, still preferably 20 25 to 60% by weight. It is impossible to formulate a

solid material when the content of the same exceeds 80% by weight. On the other hand, a content of the same lower than 5% by weight might give no effect.

The solid fat(s) may be contained in the oily
5 solid cosmetic of the present invention preferably in an amount of 5 to 60% by weight, still preferably 15 to 45% by weight. A content of the same exceeding 60% by weight might result in an insufficient spread-ability or poor adhesion. On the other hand, it is
10 impossible to form sticks or pencils when the content is lower than 5% by weight.

The weight ratio of the solid fat(s) to the volatile oil(s) is preferably 0.1 to 2, still preferably 0.2 to 1.

15 The oil-soluble polymer(s) may be preferably contained in the cosmetic of the present invention in an amount of 0.1 to 50% by weight, still preferably 1 to 30% by weight, based on the volatile oil(s). A content of the same lower than 0.1% by weight might
20 result in a poor frictional resistance while that exceeding 50% by weight might result in excessive stickiness or poor homogeneity.

The cosmetic of the present invention may be formulated by, for example, heating and mixing the
25 essential components, i.e. the oil-soluble polymer(s),

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volatile oil(s) and solid fat(s) with the use of, e.g., a homomixer, a homodisperser or a three-roll mixer followed by molding of the mixture into a desired form. The cosmetic of the present invention may be formulated
 5 into makeup products such as foundation, lipstick, eyeliner, eye shadow, eyebrow and rouge.

The flexural strength of the oily solid cosmetic thus obtained is not lower than 40g in cylindrical form of 12 mm in diameter at 25°C and preferably within a
 10 range of 150 g and 800 g considering the shape retention and the touch.

It is below disclosed that the copolymer to use here has been produced.

Referential Example 1

15 26.7 g of perfluoroalkyl methacrylate
 CH_3
 $(\text{CH}_2=\text{CCOOC}_2\text{H}_4\text{C}_8\text{F}_{17})$, 80.0 g of stearyl methacrylate
 and 30 g of toluene were introduced into a four-necked flask and dissolved and mixed therein followed by stirring at 50°C for 0.5 hour under a
 20 nitrogen gas stream. Then 1.1 g of 2,2'-azobis-2,4-dimethylvaleronitrile was added thereto and the mixture was polymerized at 65°C for five hours under a nitrogen gas stream and then at 80°C for additional one hour to thereby give a white viscous

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solution. After the polymerization, the obtained solution was diluted with toluene and poured into ethanol to thereby precipitate a copolymer product, which was then filtered and dried in vacuo. Thus

5 102.4 g of a copolymer of perfluoroalkyl methacrylate with stearyl methacrylate was obtained.

The monomer composition of the obtained copolymer was almost the same as that of the feed (the content of the perfluoroalkyl methacrylate

10 was 25.1% by weight based on F%).

Referential Example 2

The procedure of Referential Example 1 was repeated except that 50 g of perfluoroalkyl methacrylate ($\text{CH}_2=\overset{\text{CH}_3}{\text{C}}\text{COOC}_2\text{H}_4\text{C}_8\text{F}_{17}$), 50 g of stearyl

15 methacrylate, 50 g of toluene and 1.0 g of 2,2'-azobis-2,4-dimethylvaleronitrile were employed to thereby give 96.0 g of a copolymer of perfluoroalkyl methacrylate with stearyl methacrylate.

The content of the perfluoroalkyl methacrylate

20 in the polymer was 49.6% by weight and almost the same as that of the feed.

Referential Example 3

The procedure of Referential Example 1 was repeated except that 26.7 g of polyfluoroalkyl

.....25..... methacrylate ($\text{CH}_2=\overset{\text{CH}_3}{\text{C}}\text{COOC}_2\text{H}_4\text{C}_5\text{F}_{11}\text{CF}_2\text{H}$) was employed to thereby give 101.4 g of a copolymer of polyfluoroalkyl methacrylate with stearyl methacrylate.

The content of the polyfluoroalkyl methacrylate in the copolymer was 24.8% by weight and almost the same as that of the feed.

Referential Example 4

5 The procedure of Referential Example 1 was repeated except that 50 g of polyfluoroalkyl meth-
acrylate ($\text{CH}_2=\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{COOC}_2\text{H}_4\text{C}_5\text{F}_{11}\text{CF}_2\text{H}$), 50 g of stearyl
methacrylate, 50 g of toluene and 1.0 g of 2,2'-
10 azobis-2,4-dimethylvaleronitrile were employed to thereby give 97.0 g of a copolymer of polyfluoro-
alkyl methacrylate with stearyl methacrylate.

The content of the polyfluoroalkyl methacrylate in the copolymer was 50.4% by weight and almost the same as that of the feed.

15 Referential Example 5

The procedure of Referential Example 1 was repeated except that the stearyl methacrylate was replaced by behenyl methacrylate to thereby give 103.5 g of a copolymer of perfluoroalkyl meth-
20 acrylate with behenyl methacrylate.

The monomer composition of the copolymer was almost the same as that of the feed (the content of the perfluoroalkyl methacrylate was 24.9% by weight based on F%).

25 Example 1

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The solubility of rosin ester (mfd. by Arakawa Chemicals, Co., Ltd.), which was a conventional oil-soluble film-forming agent, in a volatile oil was compared with that of each copolymer of a long-
5 chain alkyl (meth)acrylate with a (meth)acrylate having a bonded fluoroalkyl group prepared in Referential Examples 1 to 5 according to the present invention in the following manner. Table 1 shows the result.

10 Solubility:

0.2 g of the rosin ester or the copolymer of the present invention and 1 g of a mixture of a low-boiling point hydrocarbon (IP Solvent 1620; mfd. by Idemitsu Oil Co., Ltd.) and a cyclic
15 dimethylpolysiloxane (SH244; mfd. by Toray Silicone Co., Ltd.) were introduced in a screwed bottle followed by sealing. The mixture was stirred at 90°C for 30 min and allowed to stand for two days. Then the dissolution state in the bottle was
20 observed with the naked eye.

Criterion:

- o : clear dissolution,
- Δ : white dispersion,
- x : separation (crystallization).

[illegible]

[illegible]

Table 1 obviously suggests that each copolymer of the present invention has an extremely high solubility and can be dispersed or dissolved in cyclic dimethylpolysiloxane having a high safety
5 by simply adding a small amount of the low-boiling hydrocarbon.

Example 2

A solution of rosin ester or each copolymer prepared in Referential Examples 1 to 5 in a
10 solvent mixture of IP1620 and SH244 of a weight ratio of 10/90 as used in Example 1 was mixed again by stirring at 90°C for 30 min. Immediately thereafter, 1 cc of the solution was dropped on a
glass plate and allowed to stand at room temperature
15 for two days. Then properties of the films thus formed on the plates were compared with each other. Table 2 shows the result.

Criterion:

- o : good,
- 20 Δ : somewhat good,
- x : poor.

Table 2

| | Appearance | Continuity | Water resistance | Oil resistance |
|------------------------|------------------------|------------|------------------|----------------|
| Rosin ester | white and crystallized | x | o | x |
| Copolymer of invention | Ref. Ex. 1 transparent | o | o | o |
| | Ref. Ex. 2 do. | o | o | o |
| | Ref. Ex. 3 do. | o | o | o |
| | Ref. Ex. 4 do. | o | o | o |
| | Ref. Ex. 5 translucent | Δ | o | o |

Example 3

Lipsticks of the following composition were produced with the use of the rosin ester and the copolymers of the present invention as a film-forming agent in the following manner. The effects of use of the obtained products were compared with each other. Table 3 shows the result.

| | Composition | parts by weight |
|----|---------------------|-----------------|
| | film-forming agent | 10 |
| 10 | IP Solvent 1620 | 7 |
| | SH244 | 49 |
| | candelilla wax | 7 |
| | ceresin | 3 |
| | pearlescent pigment | 12 |
| 15 | titanium oxide | 1 |
| | organic pigment | 1 |
| | | <hr/> |
| | | 100 |

Method for production:

Four parts by weight of IP Solvent, one part by weight of ceresin and one part by weight of the organic pigment were mixed with a roll mill to give a pigment paste. Separately the residual amount of IP Solvent, SH244, the film-forming agent, the residual amount of the ceresin and candelilla wax

were mixed by heating at 90°C and the above-mentioned pigment paste and the powder constituent were dispersed therein followed by molding in a container.

5 Method for test:

Spreadability - Each lipstick was applied on the skin and subjected to organoleptic evaluation.

Homogeneity - do.

Frictional resistance - Each lipstick was
10 applied on the skin, allowed to stand at room temperature for a sufficient period and subjected to repeated friction under a given pressure with a sponge puff. The color migration thus induced
was observed with the naked eye.

15 Water resistance - Each lipstick was applied on the skin and allowed to stand at room temperature for a sufficient period. Then water was added dropwise thereto in an amount sufficient to moisten the whole film. After 10 min, the condition was
20 observed with the naked eye.

Oil resistance - Each lipstick was applied on the skin and allowed to stand at room temperature for a sufficient period. Then liquid paraffin was added dropwise thereto in an amount sufficient to
25 moisten the whole film. After ten min, the

condition was observed with the naked eye.

Stickiness - Each lipstick was applied on the skin and allowed to stand at room temperature for a sufficient period. Then the stickiness thereof
5 was evaluated by pressing with fingers.

Criterion:

- ◎ : good,
- : somewhat good,
- △ : somewhat poor,
- 10 x : poor.

Table 3

| | on application | | Film formed after application | | | |
|-------------------------------------|----------------|-------------|-------------------------------|------------------|----------------|------------|
| | Spreadability | Homogeneity | Frictional resistance | Water resistance | Oil resistance | Stickiness |
| Lipstick of rosin ester | x | x | Δ | ⊙ | x | x |
| Lipstick of copolymer of Ref. Ex. 1 | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ | o |
| Lipstick of copolymer of Ref. Ex. 2 | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ |
| Lipstick of copolymer of Ref. Ex. 3 | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ | o |
| Lipstick of copolymer of Ref. Ex. 4 | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ |
| Lipstick of copolymer of Ref. Ex. 5 | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ | ⊙ |

The above result suggests that each cosmetic of the present invention can be homogeneously spread on application and the film formed after the application was highly resistant against friction, water and oil and showed a low stickiness. The stickiness tended to decrease with an increase in the chain-length of the alkyl (meth)acrylate or in the content of the fluorinated (meth)acrylate.

Example 4

10 An eyeliner of the following composition was produced.

| | Composition | parts by weight |
|----|--------------------------------------|-----------------|
| | copolymer of Ref. Ex. 1 | 10 |
| | IP Solvent 1620 | 8 |
| 15 | SH244 | 52 |
| | candelilla wax | 5 |
| | ceresin | 3 |
| | microcrystalline wax | 1.2 |
| | black iron oxide | 20 |
| 20 | polyoxyethylene sorbitan monolaurate | 0.2 |
| | glycerol monostearate | 0.4 |
| | perfume | 0.2 |
| | | <hr/> |
| | | 100 |

The obtained eyeliner was extremely homogeneously

spread and showed an excellent adhesion to the skin as well as high resistance against water and oil.

Example 5

A stick-type foundation of the following
5 composition was produced.

| | Composition | parts by weight |
|----|-------------------------|-----------------|
| | copolymer of Ref. Ex. 4 | 10 |
| | SH244 | 4 |
| | IP Solvent 1620 | 39 |
| 10 | candelilla wax | 10 |
| | solid paraffin | 6 |
| | cerisite | 18 |
| | yellow iron oxide | 4 |
| | red iron oxide | 2 |
| 15 | black iron oxide | 2 |
| | titanium oxide | 4.5 |
| | perfume | 0.5 |
| | | <hr/> |
| | | 100 |

The obtained foundation was extremely homogeneously spread and showed an excellent adhesion
20 to the skin as well as high resistance against water and oil with little stickiness.

Example 6

A stick-type eye shadow of the following

composition was produced.

| | Composition | parts by weight |
|----|-------------------------|-----------------|
| | copolymer of Ref. Ex. 5 | 10 |
| | IP Solvent 1620 | 4 |
| 5 | SH244 | 39 |
| | candelilla wax | 8 |
| | ceresin | 5 |
| | pearlescent pigment | 20 |
| | mica | 12 |
| 10 | titanium oxide | 1.8 |
| | perfume | 0.2 |
| | | <hr/> |
| | | 100 |

The obtained eye shadow was homogeneously spread and showed an excellent adhesion to the skin as well as high resistance against water and oil with little stickiness.

Example 7

An oily, solvent-type mascara of the following composition was produced.

| | Composition | parts by weight |
|----|-------------------------|-----------------|
| 20 | copolymer of Ref. Ex. 2 | 15 |
| | solid paraffin | 15 |
| | IP Solvent | 55 |
| | SH244 | 5 |

pigment

10

perfume

a trace amount

Method for production:

Some portion of IP Solvent, SH244 and some
5 portions of the copolymer and solid paraffin were
mixed together and dissolved by heating. Separately
the residual IP Solvent was mixed with the residual
solid paraffin and the pigment paste was added thereto.
The mixture was mixed with a roll mill and dispersed
10 in the copolymer liquid part followed by cooling.

Evaluation:

The obtained mascara applied on eyelashes was
highly resistant against water, i.e. not washed
away by tear. It was further resistant against
15 friction such as winks.

Example 8

A stick-type eyebrow of the following composi-
tion was produced.

| | Composition | parts by weight |
|----|-------------------------|-----------------|
| 20 | copolymer of Ref. Ex. 5 | 10 |
| | IP Solvent | 7 |
| | SH244 | 35 |
| | ceresin | 1 |
| | solid paraffin | 36 |
| 25 | pigment | 11 |

Method for production:

All materials other than the pigment were molten and the pigment was added and thoroughly dispersed therein. The dispersion was mixed with
 5 a heated roll mill several times, cooled to room temperature and extruded with an extruder having a nozzle of an internal diameter of 3 mm.

Evaluation:

The obtained eyebrow was resistant against
 10 water and friction and hardly deteriorated.

Example 9

A manicure of the following composition was produced.

| | Composition | parts by weight |
|----|-------------------------|-----------------------|
| 15 | copolymer of Ref. Ex. 2 | 12 |
| | nitrocellulose | 15 |
| | camphor | 6 |
| | butyl acetate | 25 |
| | ethanol | 7 |
| 20 | toluene | 30 |
| | corolant | an appropriate amount |

The obtained manicure was appropriate for application and showed an excellent adhesion to the nail.

The invention will be further illustrated with working examples in reference to the embodiment in which the cosmetic composition comprises an oil-soluble polymer, an volatile oil having a boiling point of not
5 higher than 280°C and solid fat(s) having a penetration of not higher than 40.

Example 10,

Lipsticks of the composition A as shown in Table 4 were produced in the following manner wherein polystearyl
10 methacrylate, polybehenyl methacrylate, polystearyl vinyl ether, polyisoprene, ethylene/propylene rubber or ethylene/vinyl acetate copolymer were employed as the oil-soluble polymer and low-boiling point isoparaffin (IP Solvent 1620; mfd. by Idemitsu Oil Co., Ltd.) and
15 cyclic dimethylpolysiloxane (SH-244; mfd. by Toray Silicone Co., Ltd.) were employed as the volatile oils. The effect of preventing color migration of each

lipstick was evaluated. In addition, a product containing ceresin and micaceous titanium in excessive amounts instead of the oil-soluble polymer (Composition B in Table 4) and that containing liquid paraffin instead of the oil-soluble polymer and the volatile oils (Composition C in Table 4) were produced for comparison.

Production of lipstick:

Four parts by weight of IP Solvent 1620, one part by weight of ceresin and one part by weight of red colorant No. 202 are mixed together in a three-roll mixer to give a paste. Then the whole composition was mixed in a sealed container by heating to 90°C for 30 min and poured into given molds followed by cooling at - 5°C for 20 min therein.

Evaluation of color migration:

The color migration was evaluated by applying a lipstick on 1 cm² of the human skin until the skin color could not be observed. After allowing to stand for one min, a sheet of tissue was pressed against the applied area under a given pressure, or a sheet of tissue applied on the skin was displaced laterally under a given pressure while it was pressed thereagainst. The density of the color of the lipstick migrated to the tissue by each of the above treatments was evaluated

with the naked eye according to the following criterion.

Criterion:

The color of the tissue was given point 0, while the density of the color migrated to the tissue when pressing the lipstick of Composition C with the tissue and laterally displacing the tissue while it was pressed thereagainst was given point 5.

Each lipstick was applied on 1 cm² of the human skin until the color of the skin could not be observed and allowed to stand for one min. Then a drop of liquid paraffin was placed thereon with a capillary and a sheet of tissue was pressed thereagainst. The color of the lipstick thus migrated to the tissue was evaluated according to the above criterion.

Table 4 shows the compositions of the lipsticks while Table 5 shows the evaluation of the color migration to the tissue.

Table 4

| Composition | A | B | C |
|----------------------|-------------------|-----|-----|
| | (parts by weight) | | |
| oil-soluble polymer | 10 | 0 | 0 |
| IP Solvent 1620 | 16 | 16 | 0 |
| SH 244 | 40 | 40 | 0 |
| candelilla wax | 7 | 7 | 7 |
| ceresin | 13 | 18 | 18 |
| micaceous titanium | 12 | 17 | 17 |
| titanium oxide | 0.5 | 0.5 | 0.5 |
| red colorant No. 202 | 1.5 | 1.5 | 1.5 |
| liquid paraffin | 0 | 0 | 56 |

Table 5

| Composition | Oil-soluble polymer | Pressed | Displaced | Oil drop placed followed by pressing |
|-------------|---|---------|-----------|--------------------------------------|
| A | polystearyl methacrylate (synthetic, MW: 40,000) | 0 | 1 | 1 |
| | polybehenyl methacrylate (synthetic, MW: 73,000) | 0 | 1 | 1 |
| | polystearyl vinyl ether (mfd. by BASF, Wax V) | 1 | 2 | 2 |
| | polyisoprene (mfd. by Kuraray Co., Ltd.) | 2 | 3 | 3 |
| | ethylene/propylene rubber (mfd. by Japan Synthetic Rubber Co., Ltd., EPOIP) | 2 | 3 | 3 |
| | ethylene/vinyl acetate copolymer (mfd. by Mitsubishi Petrochemical Co., Ltd., Mizette 177, containing 20.9 % by weight of vinyl acetate) | 2 | 3 | 2 |
| B | | 1 | 4 | 5 |
| C | | 5 | 5 | 5 |

The result of this evaluation, evidently shows that the cosmetic of the present invention is highly resistant against oil and exhibits a high effect of preventing color migration.

5 Example 11

The procedure of Example 10 was repeated except using a cylindrical mold of 12 mm in diameter to thereby produce a stick-type of oily foundation of the following composition and the effect of preventing color migration of the
10 same was evaluated. Further the flexural strength thereof was determined at 25°C with a rheometer (mfd. by Fudo Kogyo Co., Ltd.).

| Composition | | parts by weight |
|-------------|--------------------------|-----------------|
| | polystearyl methacrylate | 10 |
| 15 | IP Solvent 1620 | 16 |
| | SH 244 | 30 |
| | candelilla wax | 7 |
| | ceresin | 18 |
| | cerisite | 10 |
| 20 | kaolin | 5 |
| | red iron oxide | 3 |
| | yellow iron oxide | 0.5 |
| | perfume | 0.5 |
| Total | | 100 |

The obtained foundation showed an excellent spreadability while giving no driness after application and little color migration. The flexural strength thereof was 80g.

5 Example 12

A stick-type of oily eyeliner of the following composition was produced and the effect of preventing color migration and the flexural strength (25°C) of the same were evaluated.

| 10 Composition | parts by weight |
|---------------------------|-----------------|
| ethylene/propylene rubber | 10 |
| IP Solvent 1620 | 15 |
| SH 244 | 25 |
| candelilla wax | 7 |
| 15 microcrystalline wax | 18 |
| solid paraffin | 10 |
| black iron oxide | 14.5 |
| perfume | 0.5 |
| Total | 100 |

The obtained eyeliner showed and excellent spreadability and was highly resistant against sweat and sebum while causing little color migration. The flexural strength of the same was 70g.

Example 13

A pencil-type of oily eyebrow of the following

composition was produced and the effect of preventing color migration and the flexural strength (25°C) of the same were evaluated.

| Composition | | parts by weight |
|-------------|---|-----------------|
| 5 | sterayl methacrylate/perfluoroalkyl methacrylate copolymer *1 | 10 |
| | IP Solvent 1620 | 15 |
| | SH 244 | 20 |
| | candelilla wax | 12 |
| 10 | microcrystalline wax | 18 |
| | solid paraffin | 10 |
| | black iron oxide | 10.5 |
| | perfume | 0.5 |
| Total | | 100 |

- *1) A copolymer of stearyl methacrylate with perfluoroalkyl methacrylate in a weight ratio of 3/1.

$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOC}_2\text{H}_4\text{C}_8\text{F}_{17}$ was used as the perfluoroalkyl methacrylate.

The obtained eyebrow showed an excellent spreadability and was highly resistant against sebum and sweat while causing little color migration. The flexural strength of the same was 75g.

CLAIMS:

1. A cosmetic composition which comprises a copolymer of a fluoroalkyl (meth)acrylate and a straight-chain alkyl (meth)acrylate having 18 or more carbon atoms in the alkyl group.
- 5 2. A cosmetic composition which comprises a copolymer of a long chain alkyl (meth)acrylate a fluoroalkyl (meth)acrylate and a volatile oil.
3. A composition as claimed in Claim 2, in which the long chain alkyl (meth)acrylate has an alkyl group
10 having 8 or more carbon atoms.

4. A composition as claimed in Claim 2, in which the fluoroalkyl (meth)acrylate has a perfluoroalkyl or polyfluoroalkyl group with 4 or more carbon atoms in the alkyl portion.
- 5 5. A composition as claimed in Claim 2, in which the long chain alkyl (meth)acrylate has 18 or more carbon atoms in the alkyl group.
6. A cosmetic composition which comprises an oil-soluble polymer, an volatile oil having a boiling point not higher than 280°C and at least one solid fat having a penetration of not higher than 40.
- 10
7. A composition as claimed in Claim 6 in which said oil-soluble polymer is a copolymer of a long chain alkyl (meth)acrylate and a fluoroalkyl (meth)acrylate.
- 15

8. A composition as claimed in Claim 6, in which
said polymer is soluble or dispersible in the volatile
oil.
9. A composition as claimed in Claim 6, in which
5 said polymer is not compatible with the solid fat or fats.
10. A composition as claimed in Claim 6, in which said
solid fat or fats are not soluble in the volatile oil
at a temperature of 40° or lower.
11. A composition as claimed in Claim 6, which has
10 a flexural strength of 40g or more at 25°C in the
form of a cylinder having a diameter of 12 mm.
12. A composition as claimed in Claim 6, which
comprises 5 to 80 percent by weight of the volatile

oil, 5 to 60 percent by weight of the solid fat(s) and 0.1 to 50 percent by weight, based on the volatile oil, of the oil-soluble polymer.

13. A composition as claimed in Claim 6, in which said polymer is a polymer or copolymer of a vinyl monomer having a branched chain having 8 or more carbon atoms.

14. A composition as claimed in Claim 6, in which said polymer is a polymer or copolymer of (meth)acrylate, a vinyl ether, a vinyl ester or an alpha-olefin, each having 8 to 22 carbon atoms in the alkyl.

15. A composition as claimed in Claim 6, in which said polymer is a copolymer of an alpha-olefin and a maleate or a fumarate, having 8 to 22 carbon atoms in the alkyl group.

16. A composition as claimed in Claim 6, in which said polymer is an elastomeric polymer selected from polyisoprene, an ethylene propylene rubber, a copolymer of ethylene and vinyl acetate and polybutadiene.

5 17. A cosmetic as claimed in Claim 1, in which the weight ratio of the linear alkyl (meth)acrylate to the fluoroalkyl (meth)acrylate is from 7:1 to 1:1.